s-PROCESS ZIRCONIUM IN INDIVIDUAL PRESOLAR SILICON CARBIDE GRAINS

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Abstract. We have measured the zirconium isotopic composition of individual presolar SiC grains from the Murchison meteorite by resonance ionization time-of-flight mass spectrometry. All grains analyzed are strongly depleted in ^{96}Zr, the only isotope of Zr that is not normally produced by the s-process.

Introduction. Most SiC grains recovered from meteorites fall into the so-called mainstream group and have isotopic and chemical properties suggesting condensation around low-mass asymptotic giant branch (AGB) stars [1,2]. Whereas isotope ratios of a number of light elements have been measured in individual presolar grains, isotope ratios of heavy elements have only been measured in aggregates of many grains to date. Grain-size separated aggregates of presolar SiC have shown varying degrees of enrichment in the isotopes of Kr, Sr, Xe, Ba, Nd and Sm produced by s-process nucleosynthesis [1]. Since individual presolar grains may have come from different stars and from different stages of stellar evolution, measurement of heavy element isotopic compositions in presolar grains on a grain-by-grain basis is essential for further understanding of heavy element nucleosynthesis. We have developed a new instrument that combines a high sensitivity, high specificity mass spectrometer with μm-size sampling capability with the goal of isotopic analysis of single presolar grains. We chose to begin with Zr isotopic analysis of SiC grains for several reasons: (1) Zr is the most abundant heavy element in mainstream SiC grains [2]; (2) Zr has four predominantly s-process isotopes, ^{90}Zr, ^{91}Zr, ^{92}Zr, and ^{94}Zr, and one r-process isotope, ^{96}Zr; (3) because of the relatively long half-life of ^{95}Zr (64 days), the production of ^{96}Zr by the s-process is a sensitive indicator of neutron density.

Experimental. We prepared a mount in which ~200 grains of SiC grain size separate KJH (3.4–5.9 μm) from the Murchison CM2 meteorite [3] were pressed into soft gold. Mapping by scanning electron microscopy with energy-dispersive x-ray microanalysis showed that about one third of the grains in this mount are SiC; the remainder are hibonite and corundum. Isotopic analysis of Zr is challenging, because of a number of isobaric interferences from other elements that occur in presolar SiC. Zr has five stable isotopes, 90, 91, 92, 94, and 96, and has the following isobaric overlaps: Mo at masses 92, 94, and 96; Ru at mass 96; and Ti_2^+ at masses 92, 94, and 96 (with the most abundant isotope of Ti_2^+ and the least abundant isotope of Zr at mass 96). Ti and Mo are present in SiC [1,2,4] and Ru is known to be present in SiC grain-size aggregates. The mass resolution needed to resolve these interferences is beyond the capability of currently available ion microprobes. We have developed a new instrument, CHARISMA (Chicago-Argonne Resonant Ionization Spectrometer for MicroAnalysis), that gets around this difficulty by resonantly ionizing ablated or sputtered atoms of interest while leaving isobarically interfering atoms and molecules in the neutral state [5]. The operation of this instrument is described in a companion abstract on Mo isotopic measurements that were made after the Zr isotopic measurements reported here [4]. For the Zr measurements, we used a 337 nm N_2 laser for ablation; we operated at 20 Hz, the maximum repetition rate of this laser. The resonant laser radiation was generated by three XeCl excimer-pumped dye lasers: (1) 613.46 nm radiation excites Zr atoms resonantly from the a^3F_2 ground state to the intermediate $z^3F^o_2$ state; (2) 472.39 nm radiation resonantly excites Zr atoms from this state to a higher intermediate state, e^3F_2; and (3) 537.5 nm radiation ionizes the excited Zr atoms through a resonant transition to just above the ionization limit [7].

Analysis of NIST SRM 1264a steel, which contains 690 ppm Zr, 4900 ppm Mo, and 2400 ppm Ti, shows that isobaric interferences from Mo and Ti_2^+ are effectively suppressed under Zr resonance ionization conditions. Zr metal and SRM 1264a were used as isotopic standards and assumed to be of terrestrial isotopic composition. In addition, in each SiC grain, a background was measured by detuning two of the resonant lasers by 0.12 nm. In samples with nonresonant Ti^+ in their mass spectra, a small peak at mass 96 from $^{48}Ti_2^+$ was seen. Resonant spectra were corrected for this interference, normalizing to the $^{48}Ti^+$ peak in both resonant and detuned spectra.

Results and discussion. Approximately 30 grains in the KJH mount were ablated in CHARISMA. Of these, 11 had Zr concentrations high enough to make isotopic measurements. In addition to the individual grains, we also analyzed an aggregate sample of Murchison separate KJB, which has a grain size range of 0.32–0.70 μm [3]. All SiC samples analyzed show large depletions in ^{96}Zr (Fig. 1). One sample shows a δ^{96}Zr value of less than –1000 ‰. This is clearly im-

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possible and is an artifact of the correction of ^{96}Zr for nonresonant Ti_2^+; this grain has no detectable ^{96}Zr.

Also shown in Fig. 1 are evolutionary tracks for successive third dredge-up episodes for 1.5 and 3 solar mass AGB stars with twice the solar metallicity [7]. The agreement with the SiC grains is quite good, considering the uncertainties in the Zr isotopic measurement. Not only are large ^{96}Zr deficits predicted and observed, but also, small deficits in ^{90}Zr and excesses in ^{94}Zr are predicted and observed. Only for ^{91}Zr is an excess predicted and perhaps a small deficit observed. The primary neutron source for the *s*-process is $^{13}C(\alpha,n)^{16}O$ [8]. The size of the ^{13}C pocket in these calculations is arbitrary and was chosen to provide the best match with the light element isotopic compositions of mainstream SiC grains [7]. ^{90}Zr, ^{91}Zr, ^{92}Zr, and ^{94}Zr are produced and ^{96}Zr is consumed by the *s*-process. In the later thermal pulses, the bottom of the convective shell becomes hot enough to activate the $^{22}Ne(\alpha,n)^{25}Mg$ reaction, producing a higher neutron density. Under these conditions, ^{95}Zr can capture a neutron to form ^{96}Zr before beta decay occurs, causing the turnaround in the calculated trajectories. A number of SiC grains have ^{96}Zr deficits larger than predicted by these calculations, suggesting that either the ^{22}Ne neutron source is not important in the AGB stars where these grains formed or that poorly-mixed pockets of *s*-process material can reach the outside of the convective envelope of AGB stars to be ejected and condense into grains. SiC grains must, of course, condense around the star from material ejected from the envelope. The trajectories in Fig. 1 start with solar isotopic composition and reflect mixing in of increasing amounts of *s*-process nucleosynthesis products. The C/O ratio increases with successive third dredge-up episodes. On Fig. 1 the symbols along the tracks change from closed to open when the C/O ratio exceeds 1 and SiC can condense. A number of the SiC grains have ^{96}Zr deficits expected for grains that would have formed during the O-rich portion of AGB evolution. This may also place constraints on mixing processes in AGB star envelopes.

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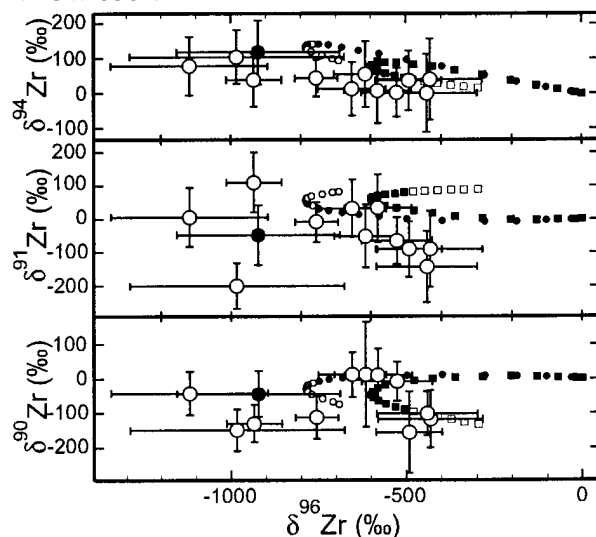
Fig. 1. Zr isotopic compositions ($\pm 2\sigma$) of 3.5–7.5 μm individual presolar SiC grains (large open circles) and an aggregate of 0.32-0.70 μm SiC grains (large closed circle) , normalized to ^{92}Zr and to terrestrial Zr isotopic composition. Also shown are evolutionary tracks for 1.5 (small circles) and 3 (small squares) solar mass AGB stars [7]. The symbols along the AGB tracks change from closed to open when the C/O ratio exceeds 1 and SiC can condense.